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ELECTRON MICROSCOPE INVESTIGATIONS OF FROZEN AND UNFROZEN BENTO--ETC(U)
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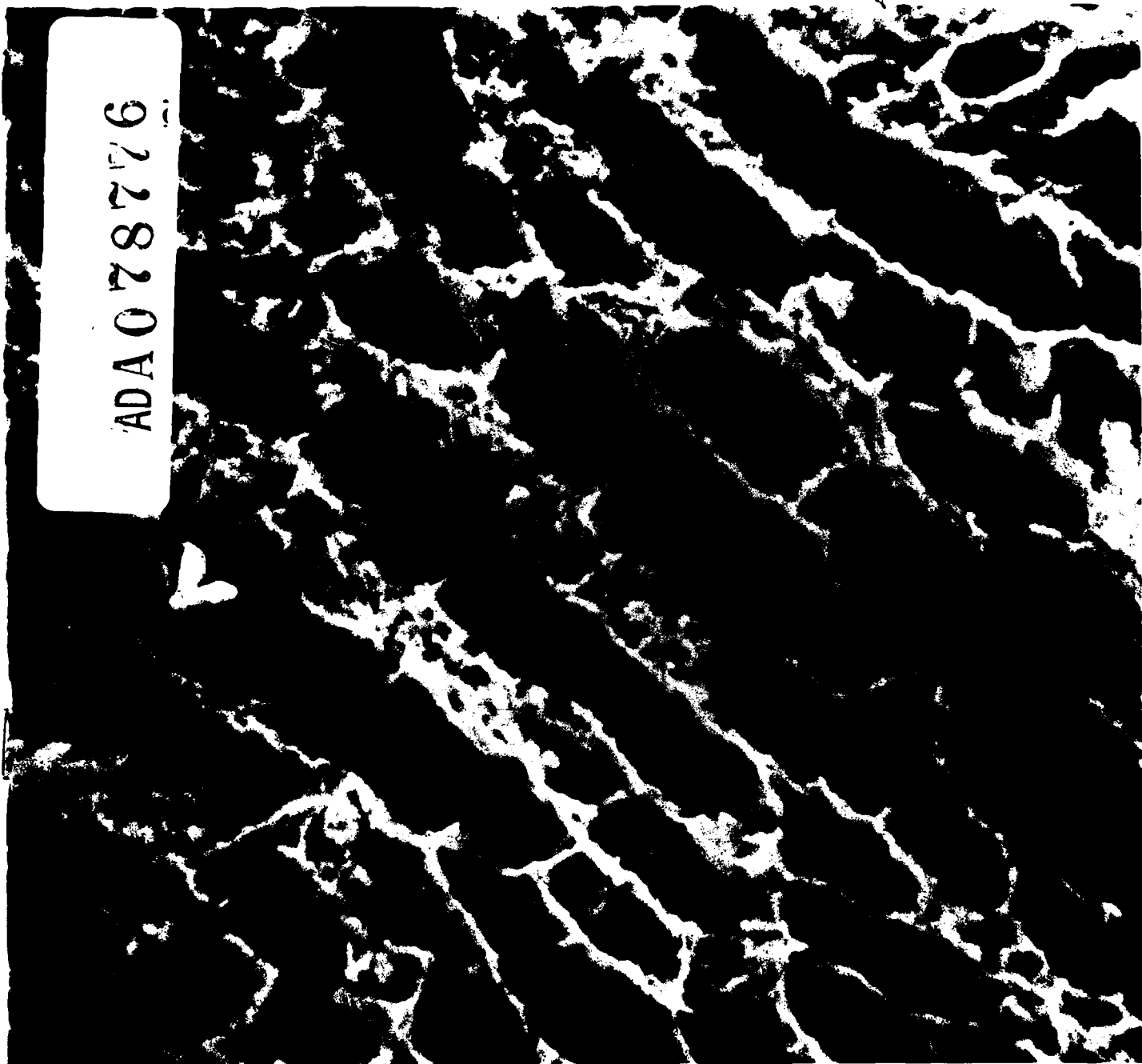
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Electron microscope investigations of
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Cover: Scanning electron micrograph of frozen
Umiat bentonite, magnification X700.
(Photograph by M. Kumai.)

CRREL Report 79-28



Electron microscope investigations of frozen and unfrozen bentonite

Motoi Kumai

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Transmission and scanning electron micrographs of Umiat bentonite revealed thin, mica-like grains with irregular shapes. Most of the bentonite showed electron diffraction ring patterns, but some showed hexagonal net patterns as well as ring patterns. The lengths of the unit cells were calculated to be 5.18 Å along the a-axis and 8.97 Å along the b-axis. Semiquantitative analyses were made using an energy dispersive spectrometer. Common elements such as Si, Ti, Al, Fe, Mg, Na and K were determined. The molecular ratio of SiO ₂ :Al ₂ O ₃ was calculated to be 492:100 for the bulk sample, indicating that Umiat bentonite is similar in most respects to Wyoming bentonite, and is classified as a montmorillonite. The microstructure of frozen Umiat bentonite was observed at a specimen temperature of -100°C using a scanning electron microscope equipped with a cold stage. Frozen bentonite and segregated ice patterns formed from		

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20. Abstract (cont'd).

Wet bentonite were examined using an X-ray map and Si X-ray line scan. Sublimation processes of ice in the frozen bentonite were observed at specimen temperatures of -60° and -80° C. After sublimation of the ice the bentonite displayed a honeycomb structure. It was concluded that the freezing-sublimation cycle in frozen soil increases the permeability of water vapor due to the three-dimensional structure of the coagulated clay formed by freezing.

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PREFACE

This report was prepared by Dr. Motoi Kumai, Research Physicist, of the Physical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. The work covered by the report was conducted under DA Project 4A161102AT24, *Research in Snow, Ice, and Frozen Ground, Scientific Area A, Properties of Cold Regions Materials, Work Unit 003, Microstructure of Cold Regions Materials*.

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ELECTRON MICROSCOPE INVESTIGATIONS OF FROZEN AND UNFROZEN BENTONITE

Motoi Kumai

INTRODUCTION

This paper presents the results of measurements of the lattice spacing, unit cell length, chemical species, and molecular ratio of silica to alumina of Umiat bentonite made using a transmission electron microscope, electron diffraction, and an energy dispersive X-ray analyzer. It describes the microstructure of the frozen soil, the ice/clay interface, and sublimation processes of ice in frozen Umiat bentonite determined with a scanning electron microscope equipped with a cold stage and a built-in temperature control and thermocouple.

Studies of the physical properties of clays and clay minerals have been carried out by many workers. Hayashi (1978) examined the morphological, structural and chemical characteristics of individual clay minerals using a transmission electron microscope with an energy dispersive spectrometer. The results of energy dispersive analyses of these clay minerals were compared with the results of chemical analyses. It was concluded that energy dispersive analyses were satisfactory for characterizing clay minerals.

The morainic soils of continental Antarctica have formed in a severely cold and arid climate. Morainic soils in the lower Wright Valley and in Beacon Valley, southern Victoria Land, were investigated using a scanning electron microscope and an energy dispersive X-ray

analyzer by Kumai et al. (1978). The Wright Valley soils had grains with sharp edges and fresh, smooth surfaces, indicating a low degree of weathering. The Beacon Valley soils showed salt efflorescence on rounded grains, indicating a high degree of mechanical and chemical weathering. It was concluded that the soils from the Wright Valley were much younger than those from the Beacon Valley.

In a laboratory experiment, vertical and horizontal thin sections of frozen soil were examined by Chamberlain and Gow (1978). They found that development of ice lenses in Morin and Ellsworth clays was greater than that of CRREL clay and Hanover silt at low applied stress. Polygonal ice patterns were found in horizontal thin sections of frozen Morin and Ellsworth clays.

The name *montmorillonite* was given by Damour and Salvétat (1847) to a clay mineral from Montmorillon, France. Nontronite, beidellite, hectorite, and saponite are related structurally to it and belong to the montmorillonite group. The nomenclature of the montmorillonite clay mineral is now reasonably well defined. A comprehensive modern survey and bibliography has been published by MacEwan (1961).

The name *bentonite* was originally proposed for a clay from Rock Creek, Wyoming (Knight 1898). The clay is micaceous in nature, with

facial cleavage and a texture inherited from volcanic ash, and it is one of the montmorillonite group.

Bentonite beds in northern Alaska were reported by Detterman et al. (1963). The beds are 25 to 30 cm thick, and are conveniently accessible at Umiat Mountain, 6½ km northeast of the village of Umiat. X-ray diffraction, X-ray fluorescence and other diagnostic techniques have revealed that this bentonite is nearly pure montmorillonite with certain beidellitic characteristics (Anderson and Reynolds 1966).

A scanning electron microscope equipped with a cold stage was used by Echlin et al. (1970) and Nei et al. (1971) to examine biological specimens. The freeze-dry method allowed these specimens to be maintained in their natural state. The method is also considered to be suitable for studying the microstructure of frozen soils. A study of the microstructure of frozen Umiat bentonite has not yet appeared in the literature.

MATERIAL AND METHOD

The bentonite was collected at Umiat, Alaska, by D. Anderson and A. Tice (Anderson and Reynolds 1966). In this investigation, it was selected as a typical swelling clay of the cold regions with a mica-like nature and a thin, irregular shape. Our laboratory examination included terrestrial samples and treated samples. Specimens were prepared at 10, 50 and 75% weight concentration of clay to water.

Transmission electron microscopy

Electron photomicrographs and selected area diffraction patterns of Umiat bentonite were obtained with an RCA-3F electron microscope operated at an accelerating voltage of 100 kV. The bentonite particles, which were less than 2 µm in diameter, were suspended in distilled water, and a 5-µl drop of the suspension was placed on a collodion film supported by a 200-mesh copper grid. The suspension was evaporated in a desiccator and shadowed with chromium vapor at an angle of 18°25' in a vacuum chamber. The specimen was then introduced into the specimen stage of the electron microscope for examination.

Scanning electron microscopy

A Hitachi S-500 scanning electron microscope

equipped with a cold stage (Fig. 1) and an energy dispersive X-ray analyzer was used in this experiment. A specimen was placed in a hole 3 mm in diameter on the specimen holder and rapidly frozen by immersing it in liquid nitrogen. The specimen holder and frozen specimen were then fixed to the specimen exchange rod and inserted into a pre-evacuation chamber. The chamber was quickly evacuated to a pressure of 1×10^{-5} torr. The frozen specimen was then immediately transferred onto the cold stage, which had previously been cooled by liquid nitrogen. The specimen exchange rod was removed from the cold stage and the airlock shutter between the pre-evacuation chamber and the main column was closed.

During operation of the scanning electron microscope the frozen soil specimen may be cooled by the latent heat of sublimation of ice, and it may be warmed by absorption of the electron beam. The specimen temperature is therefore difficult to measure. However, the temperature of the cold stage close to the specimen is considered to reflect the specimen temperature to within a few degrees Celsius. This temperature was measured throughout the entire process of frozen soil observation using a built-in copper-constantan thermocouple. The temperature of the cold stage was controlled by a built-in heater with an output of 0 to 100 V and a maximum current of 1 ampere. All temperatures given in this paper are therefore those of the cold stage.

The ultimate vacuum of the scanning electron microscope is 5×10^{-6} torr. This is the saturation vapor pressure of ice at -86.9°C, as shown in Figure 2. Therefore scanning electron photomicrographs of the frozen soil were taken below this temperature and the sublimation processes of ice in the soils were studied above it.

The cold stage temperature ranged from -125°C to -60°C during the experiments. The working distance of the cold stage was 15 mm and the tilt angle of the specimen was 0° or 30°. The accelerating voltages of the scanning electron microscope were 5, 10 and 20 kV.

RESULTS

Size of soil grains

Twenty-six transmission electron micrographs of Umiat bentonite were obtained and the diameter and thickness of the grains were

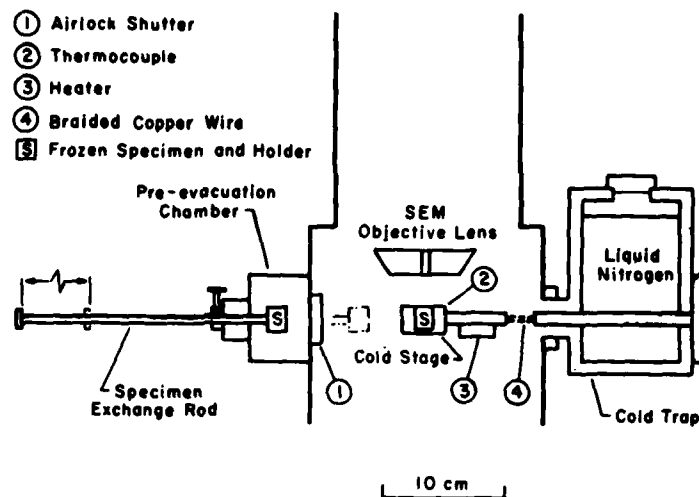


Figure 1. Schematic illustration of scanning electron microscope equipped with cold stage.

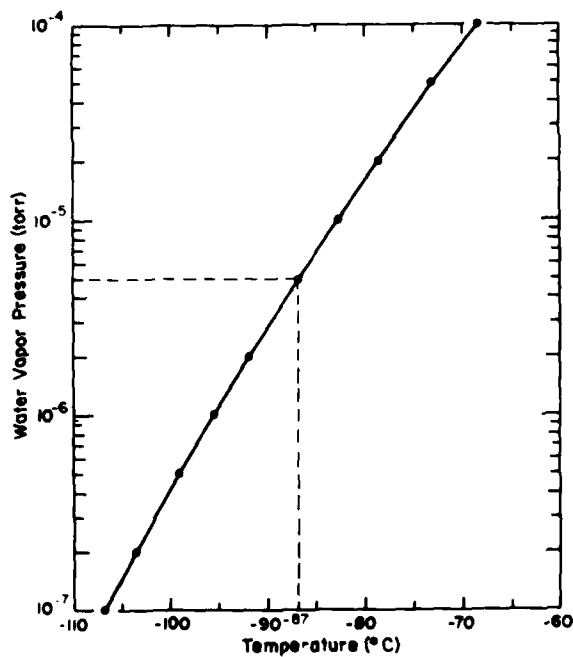
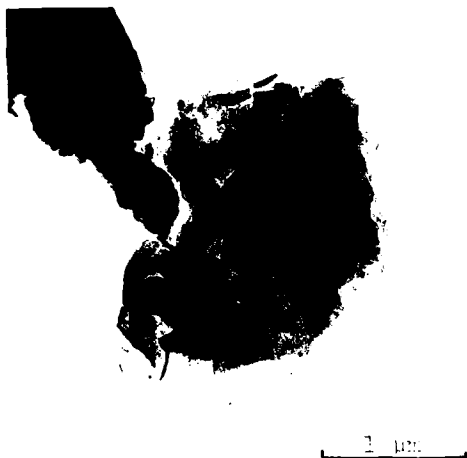
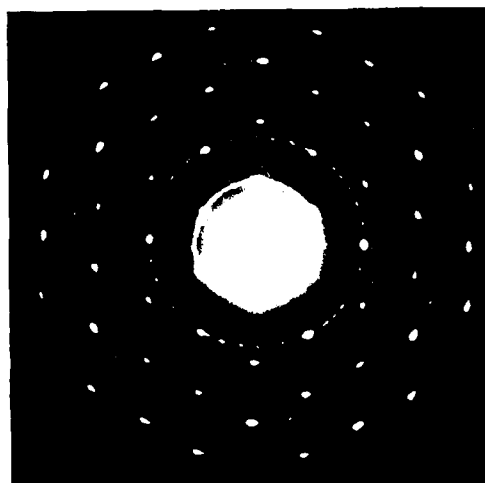


Figure 2. For a frozen soil specimen on the cold stage of the scanning electron microscope, ice sublimation occurs at temperatures above -87°C .



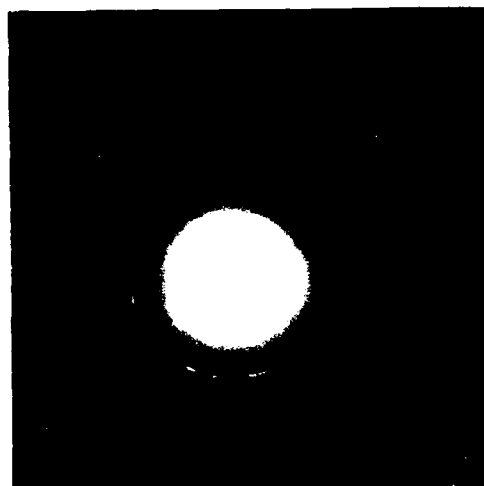
a. Umiat bentonite



b. Electron diffraction pattern of bentonite in a.



c. Umiat bentonite shadowed by Cr vapor.



d. Electron diffraction pattern of bentonite in c.

Figure 3. Transmission electron photomicrographs and selected area electron diffraction patterns of Umiat bentonite.

measured. The grains exhibited mica-like cleavage (Fig. 3a) and irregular shapes (Fig. 3a and c). They ranged from 0.1 to 2.0 μm in diameter. The size distribution obtained from 250 grains is shown in Figure 4. The mean diameter was calculated to be 0.6 μm . The thickness of the grains (Fig. 3c) was measured from the length of their shadows, being one-third the length of the shadow at the shadowing angle of $18^\circ 25'$ in the vacuum chamber. The measured thickness ranged from 20 to 2000 \AA .

Lattice constant

The selected area electron diffraction patterns of the bentonite were recorded on photographic plates at room temperature. The camera constant λL can be obtained for the standard substance by the relation of a Bragg reflection,

$$\lambda L = rd$$

where λ is the electron wavelength at an accelerating voltage of 100 kV, L is the camera length, r is the radius of the ring patterns from the (h, k, l) plane, and d is the spacing of the (h, k, l) plane. The camera constant was obtained from a standard substance, sodium chloride or gold, which was shadowed in a vacuum chamber on one part of a thin collodion film. In this experiment, the camera constant was

$$\lambda L = 7.920 (\text{\AA cm}).$$

In these experiments, 19 selected area electron diffraction patterns were obtained. The pattern in Figure 3b, obtained from the central portion of the grain of Umiat bentonite in Figure 3a, shows a superimposed electron diffraction pattern with hexagonal net and ring patterns. This indicates that the bentonite is well crystallized. Figure 3d is the diffraction pattern of the central grain shown in Figure 3c; only ring patterns appear. The majority of the grains showed only ring patterns, which indicates that the grain has a smaller crystalline structure than a grain producing hexagonal net patterns.

The d-spacings of the two specimens (Fig. 3a and 3c) were obtained from the measured radii of the ring patterns (Fig. 3b and 3d) and the Bragg relation. The ortho-hexagonal (h, k, l) index and d-spacing of the two specimens are shown in Table 1. In Table 1, the calculated values of the d-spacing for ortho-hexagonal indexes are based

on $a = 5.18 \text{\AA}$ and $b = 8.97 \text{\AA}$. The standard deviation of the d-spacing was $\pm 0.01 \text{\AA}$, based on reflections from d_{020} through d_{040} . In Table 1, the d_{060} spacing of 1.50\AA indicates that the Umiat bentonite is dioctahedral.

Semiquantitative chemical analysis

Chemical analysis of each grain and the bulk sample of Umiat bentonite was carried out using an energy dispersive X-ray spectrometer. The incident electron beam generates a characteristic X-ray of elements in the specimen. The intensity I of the characteristic X-ray is

$$I = k\phi w$$

where k is a constant, ϕ is the incident beam intensity, and w is the mass of the element in the irradiated area. Marshall and Hall (1968) reported that the concentrations of elements can be obtained by measuring their characteristic X-ray intensities. The relative peak intensity ratio of each element was calculated from

$$n_1\text{Na} + n_2\text{Mg} + \dots + n_i\text{X}_i = C$$

where n_i is the ratio of net peak intensity to the total X-ray intensity. The numerical value C neglects the water content.

A scanning electron photomicrograph of a broken surface of the bulk sample of Umiat bentonite shows the crumpled and folded structures of grains of the bentonite (Fig. 5a). Its energy dispersive X-ray pattern is shown in Figure 5b. The results of chemical analysis of the bulk sample of Umiat bentonite are shown in Table 2. These results agreed within experimental error with the analysis of the $<2 \mu\text{m}$ fraction of Umiat bentonite using the X-ray fluorescence method as shown in Table 2.

The molecular ratio of silica (SiO_2) to alumina (Al_2O_3) of the bentonite was calculated for two kinds of samples from their weight percent, shown in Table 2. The molecular ratio was calculated to be $(\text{SiO}_2:\text{Al}_2\text{O}_3)$ 492:100 for the terrestrial bulk sample and 503:100 for the $<2 \mu\text{m}$ fraction sample.

Microstructure of frozen soil

Effect of freezing temperature

Scanning electron micrographs of frozen Umiat bentonite in 10, 25, 50 and 75% weight concentrations of clay to water were taken, with the magnification being varied from $\times 50$ to

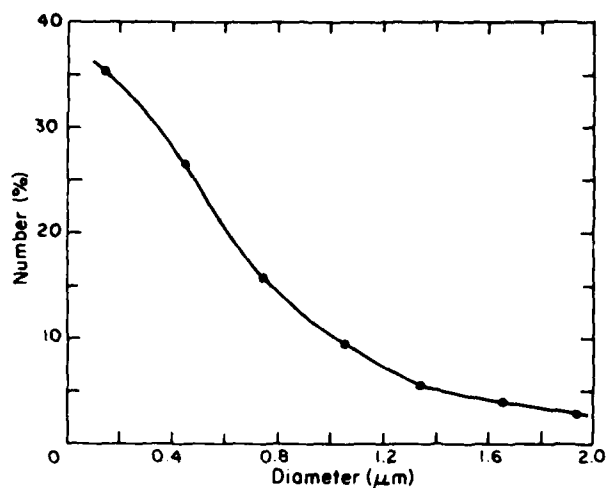


Figure 4. Grain size distribution of Umiat bentonite.

Table 1. Selected area electron diffraction data for Umiat bentonite

Diffraction pattern					
Ortho-hexagonal (h, k, 0) index	Fig. 3b		Fig. 3d		$d(\text{\AA})_{\text{calc}}$
	$d(\text{\AA})_{\text{obs}}$	I_{obs}	$d(\text{\AA})_{\text{obs}}$	I_{obs}	
020	4.50	vs	4.51	vs	4.499
200	2.59	vs	2.58	vs	2.597
040	2.25	m	2.24	m	2.249
240	1.71	m	1.70	m	1.700
060	1.50	m	1.51	m	1.499
400	1.29	m	1.29	m	1.299
420	1.25	m	1.25	vw	1.248
080	1.125	w	1.125	vw	1.125

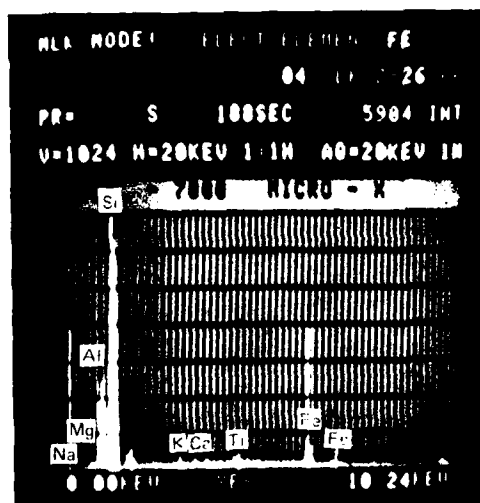
vs = very strong, m = medium, w = weak, vw = very weak

Table 2. Major element analyses for < 2 μm fraction clay and terrestrial bulk samples of Umiat bentonite (wt % oxides, neglecting H₂O)

Method	Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ +FeO	MgO	CaO	Na ₂ O	K ₂ O	References
X-ray fluorescence	< 2 μm	55.99	0.15	18.92	3.38	3.08	1.61		0.08	Anderson & Reynolds 1966
Energy dispersive X-ray analysis	bulk	52.90	0.65	18.28	3.56	2.61	1.63	1.19	1.26	This paper



a. Terrestrial sample of Umiat bentonite.



b. Energy dispersive X-ray analysis of bentonite in a.

Figure 5. Scanning electron photomicrograph and energy dispersive X-ray analysis of bulk sample of terrestrial Umiat bentonite.



Figure 6. Scanning electron photomicrograph of frozen Umiat bentonite (10% clay, 90% water by weight) at -100°C .

$\times 5000$ at intervals of about 3 minutes. In total, 103 scanning electron photomicrographs, two Si X-ray maps, and five Si X-ray line analyses of these frozen samples were obtained.

Specimens of frozen soils made at -10°C and -190°C were observed to determine their structures. Specimens were frozen in a cold chamber at -10°C . The structures of the frozen soil surfaces were observed under the optical microscope at a magnification of $\times 50$. Other specimens were immersed in liquid nitrogen (-190°C) and transferred into the cold stage in the scanning electron microscope. Scanning electron micrographs of the frozen soil were taken at a magnification of $\times 50$. Soil frozen at -10°C showed the same structure as soil frozen at -190°C (Fig. 6). The effect of the different freezing temperatures on the microstructure of the frozen soils was negligible for these bentonite specimens.

The specimen prepared with 10% by weight Umiat bentonite and 90% water was paste-like with a low viscosity. Scanning electron micrographs of the specimen taken at -100°C using the cold stage are shown in Figure 7. Figure 7b is a Si X-ray map of the area shown in Figure 7a. The white spots in Figure 7b show the location of the frozen soil. The dark (unspotted) areas are ice that became segregated from the paste-like soil during freezing. The photomicrograph of frozen soil in Figure 7c is overprinted with a line (x) along which a Si X-ray scan was

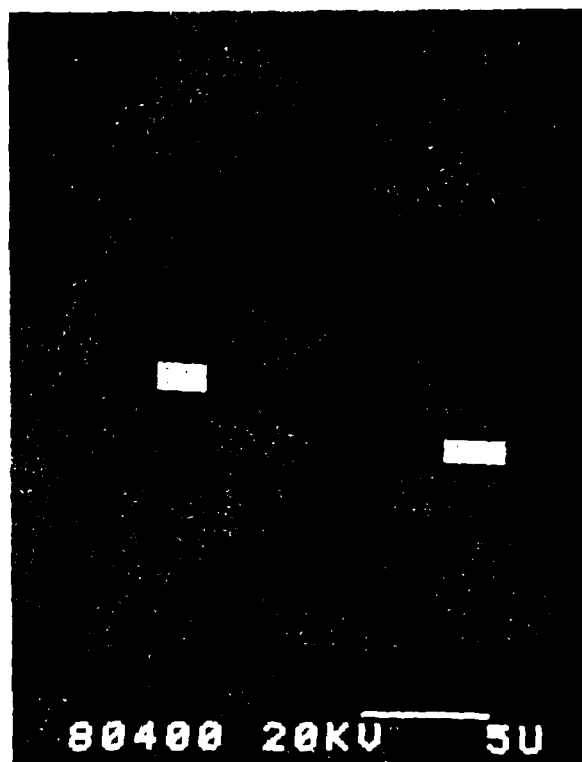
made, and the line scan itself (y). The line scan indicated that the frozen soil is a Si compound, and the dark area is ice that became segregated from the soil-water paste during the freezing process. The effect of freezing temperatures on the paste-like bentonite samples was generally small.

Effect of sublimation temperature

A specimen of Umiat bentonite was prepared by mixing 10% clay and 90% water by weight. The specimen was frozen from the surface inward by immersing it in liquid nitrogen. The surface morphology of the frozen soil was observed under the scanning electron microscope. The scanning electron micrograph in Figure 8a, taken at -100°C , shows frozen soil and segregated ice. The specimen temperature was raised to -60°C to allow the process of sublimation of ice in frozen soil to be observed. During ice sublimation, minute grains of frozen bentonite were coagulated, and then mica-like bentonite (Fig. 8b) was formed. Figure 8b shows that the interlamellar water in the frozen bentonite was sublimed at -60°C . The segregated ice in the frozen bentonite was sublimed, and cavities formed at the locations of the segregated ice. A Si X-ray map (Fig. 8c) of the frozen bentonite was obtained after sublimation of the ice at -60°C (Fig. 8b). The Si X-ray map indicates that the ice in the frozen bentonite was completely sublimed.



a. Frozen Umiat bentonite

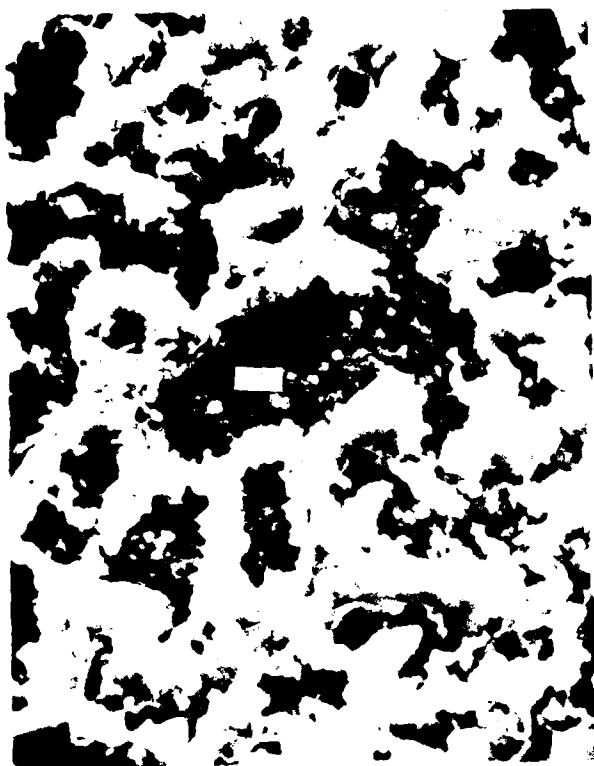


b. Si X-ray map of specimen in a.



c. Line scan.

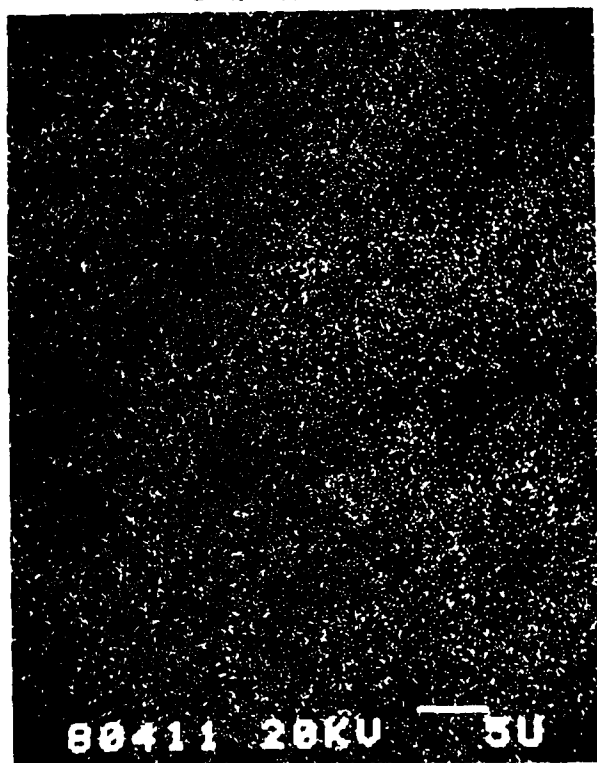
Figure 7. Frozen Umiat bentonite (10% clay, 90% water by weight), its energy dispersive Si X-ray map, and the Si X-ray line scan.



a. At -100°C .



b. After sublimation of ice at -60°C .



c. Si X-ray pattern of specimen in b.

Figure 8. Process of sublimation of ice in frozen Umiat bentonite (10% clay, 90% water by weight) at -60°C

Structure of the fracture surface in frozen soil

Specimens of 10% Umiat bentonite and 90% water by weight were prepared and frozen at the temperature of liquid nitrogen. The frozen soil specimen was mounted on the cold stage and broken. The fracture surface was observed under the scanning microscope, and photomicrographs were taken to examine the microstructure. A photomicrograph of the fracture surface (Fig. 9a) shows the frozen bentonite pattern (white) and segregated ice pattern (dark). The temperature of the frozen soil was kept at -80°C . The ice in the frozen soil sublimed slowly, forming cavities. The soil structure of the frozen Umiat bentonite (Fig. 9b) was maintained in its original state without loss of the interlamellar water. The surface structure (Fig. 6) and fractured surface structure (Fig. 9) of the frozen bentonite were almost the same.

Effect of water content in soils

Specimens were prepared at 10, 50 and 75% by weight concentrations of Umiat bentonite to water. The specimens were then immersed in liquid nitrogen and observed on the cold stage in the scanning electron microscope. Frozen soil with 10% bentonite showed a three-dimensional honeycomb structure (Fig. 9b). The bentonite specimen with 50% water content was a paste-like gray gel. The surface morphology of the frozen soil on the cold stage was observed under the scanning electron microscope at a specimen temperature of -80°C . The pattern of frozen soil and segregated ice formed during rapid freezing is shown in Figure 10a. Air bubbles are visible in the ice. At a specimen temperature of -80°C , the segregated ice was slowly sublimed from the frozen bentonite. A cavity was formed, the bottom of which is clearly visible in Figure 10b. The microstructure of the frozen soil remained the same during ice sublimation, as can be seen in Figures 10a and b. The crumpled and folded structure of the grains of frozen bentonite can be seen in both photographs. The folded structure of the grains of frozen bentonite (Fig. 10a) is similar to that of the dry bulk sample (Fig. 4a).

Segregated ice in the frozen bentonite increased with increasing water content. Frozen bentonite specimens with high water contents had three-dimensional honeycomb patterns (Fig. 9b), which formed by coagulation of the bentonite grains due to freezing. However, frozen bentonite of lower water content showed no honeycomb structure (Fig. 10a).

SUMMARY AND CONCLUSIONS

Transmission electron micrographs of Umiat bentonite revealed a thin clay with a mica-like nature. This same type of clay appeared in the electron micrographs of a fracture surface of the terrestrial bulk sample of Umiat bentonite.

Most of the grains of Umiat bentonite showed electron diffraction ring patterns (Fig. 3c and d), but some grains showed hexagonal net patterns, indicating that they were well crystallized (Fig. 3a and b).

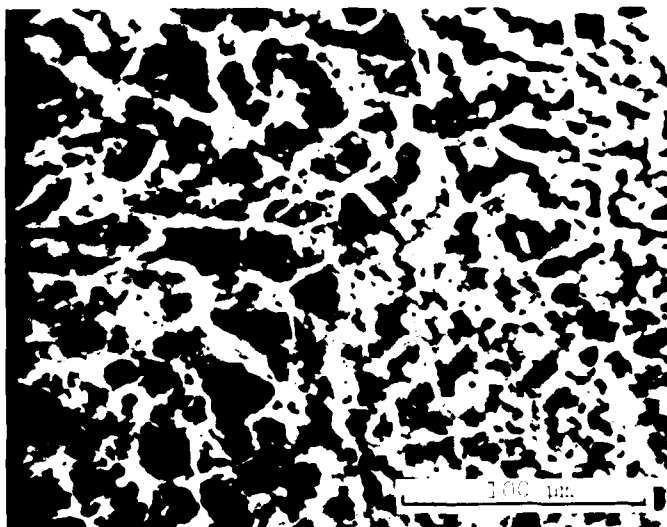
From measurements of selected area diffraction patterns obtained from Umiat bentonite (Table 1), the length of the a-axis of the unit cell was calculated to be 5.18 \AA and that of the b-axis to be 8.97 \AA for an orthohexagonal cell. The electron diffraction data for Umiat bentonite agree well with those for montmorillonite (MacEwan 1961).

The molecular ratio of Umiat bentonite ($<2 \mu\text{m}$ fraction) was calculated to be $\text{SiO}_2:\text{Al}_2\text{O}_3 = 503:100$ from the element analyses (Table 2) in this experiment. The ratio of the bulk sample of terrestrial Umiat bentonite was calculated to be $\text{SiO}_2:\text{Al}_2\text{O}_3 = 492:100$ from the element analyses (Table 2). The ratio of montmorillonite 23, from Chambers, Arizona, was calculated to be $\text{SiO}_2:\text{Al}_2\text{O}_3 = 478:100$ from the chemical analysis data (Kerr et al. 1950).

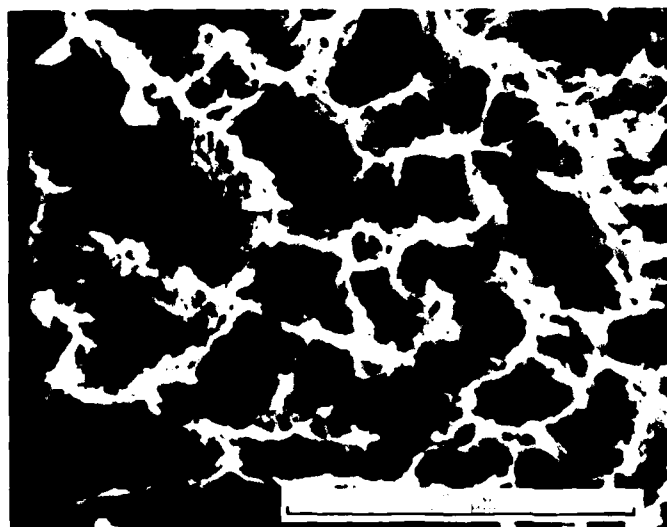
Beidellite has been placed in the montmorillonite group. However, its silica:alumina molecular ratio is different. The silica:alumina molecular ratio for montmorillonite is about 400:100 and that for beidellite is about 300:100 (Kerr et al. 1950). The ratio for Umiat bentonite, 492:100, is closer to that of montmorillonite than to that of beidellite in this examination.

Scanning electron micrographs of frozen Umiat bentonite (10% clay, 90% water; 25% clay, 75% water; 50% clay, 50% water; 75% clay, 25% water by weight) were taken at various magnifications to observe 1) its surface microstructure and fractured surface, 2) the effect of freezing temperature and water content, and 3) ice sublimation.

Specimens of Umiat bentonite (10% clay, 90% water by weight) are gray paste-like clay suspensions with low viscosity. Specimens were frozen at -10°C and observed under an optical microscope at the same temperature. Specimens frozen at about -190°C were observed on the cold stage in the scanning electron microscope at temperatures from -100°C to -60°C . When

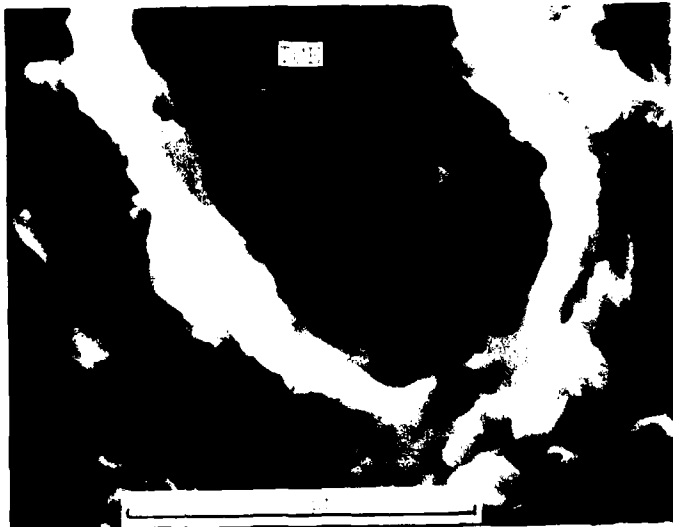


a. Fracture surface at -80°C .

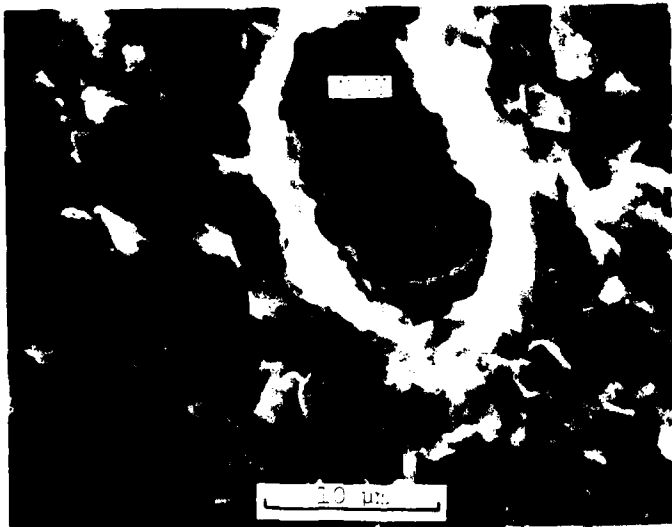


b. Fracture surface that appeared on sublimation of ice at -80°C .

Figure 9. Process of sublimation of ice in fractured sample of frozen Umiat bentonite (10% clay, 90% water by weight) at -80°C .



a. At -80°C.



b. Sublimation of ice in the frozen soil at -80°C.

Figure 10. Process of sublimation of ice in frozen Umiat bentonite (50% clay, 50% water by weight) at -80°C.

the specimens are freezing, ice is segregated from the paste-like bentonite. In the freezing stage, the swelling bentonite coagulates. The structure of frozen bentonite (Fig. 7a) is irregular in shape. The surface microstructure of bentonite frozen at -10°C showed a structure similar to that of a specimen (Fig. 6) frozen at -190°C .

The surface structure of the frozen Umiat bentonite (Fig. 8a) was similar to that of the fractured specimen (Fig. 9a), i.e. the structures of the surface and the inside were similar.

The temperature of the bentonite was kept at -80°C in the scanning electron microscope. The segregated ice in the frozen bentonite was slowly sublimed, and cavities (Fig. 9b) were formed. The structure of frozen bentonite is irregular in shape and resembles a honeycomb (Fig. 9b) at -80°C .

The temperature of the specimen was raised to -60°C and minute grains of frozen bentonite were coagulated again by subliming the ice. A mica-like bentonite (Fig. 8b) was formed.

At higher water contents the honeycomb structure in the frozen bentonite was better developed. It is concluded that the freeze-ice sublimation cycle in frozen bentonite increases the permeability of water vapor due to the three-dimensional structure of coagulated clay formed by freezing.

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